INTERACTION OF SO_x AND NO_x WITH SOOT

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INTRODUCTION

As part of a continuing study of the heterogeneous reactions of black carbon with gas phase oxidant species, the adsorption of low concentrations (30 - 2000 ppm) of SO_2 and NO_2 individually, together, and in the presence of other adsorbates have been studied by spectroscopic and microgravimetric techniques. Previous work in this study has revealed a dual path mechanism for the reaction of NO_2/N_2O_4 with n-hexane soot over concentration range 9 ppm - 200 torr (1,2). (This soot has been used throughout these investigations as a model for fossil fuel-produced black carbon). The effect of simulated solar radiation on the reaction at lower pressures (9-35ppm) is in the diminution of the NO_2 reactant through its photolytic dissociation (2). An FT-IR study of the reaction of various nitrogen oxides with black carbon showed the only reactive species at 298K to be NO_2, with NO and N_2O unreactive (3). A spectroscopic examination of the gaseous products of the soot-oxides of nitrogen-water vapor reaction has revealed the formation of CO, CO_2, and N_2O, along with NO, from a redox reaction between NO_2/N_2O_4 and the most reactive components of soot during the reaction's early stages (4). At higher temperatures and NO_2/N_2O_4 pressures, n-hexane soot undergoes chemisorption and two types of redox reaction depending upon the conditions (5). The major redox reaction, for which an intermediate $C-(NO_2)x$ complex has been identified, is precluded by prior chemisorption but, if initiated, results in brisk oxidation of the carbon to CO and CO_2 (5). Previous studies of black carbon-SO_2-H_2O-O_2 reaction systems in these laboratories include the effect of simulated solar radiation in the formation of surface sulfate (6) and the effect of metal oxides with carbon on sulfate formation (7). Interaction of SO_2 and carbon represent the most intensively studied of the heterogeneous systems containing carbon. An attempt to understand the molecular dynamics involved in the reactions of carbon in the presence of multiple reactants, such as SO_2 and NO_2, underlies the present work.

RESULTS AND DISCUSSION

SO_2 Adsorption

Because those reactions of SO_x and NO_x in the presence of and with black carbon which are of interest to us occur in air, all adsorption studies were carried out in the presence of zero air (compressed air with CO_2 and H_2O removed). This immediately raises the question of any role of O_2 in SO_2 adsorption, one addressed in our other paper in this symposium (8), involving competition for adsorption sites. That work demonstrates no such direct competition, or at least weaker adsorption of SO_2, the presence of SO_2 showing no effect on the corrected normalized integral of soot's EPR signal (8).

Microgravimetric experiments in which 10 mg n-hexane soot was exposed to 600-2000 ppm SO_2 show a depletive adsorption as illustrated in Figure 1. At 60 min., just prior to the purge with zero air, the surface coverages (θ) by SO_2 were calculated from soot mass increase, its specific surface area of 89±2 m^2/g, and a molecular area for SO_2 of 19.2 $Å^2$(9), for each replicate run. A plot of θ versus P_{SO2} shows a linear dependence, Figure 2, for which the relationship

$$\theta = (5.06 \pm 0.07) \times 10^{-5} P_{SO2} + (18.16 \pm 0.08) \times 10^{-2} \quad (1)$$

obtains. A linear relationship between θ and P is expected at low pressures for adsorption systems obeying the Langmuir isotherm (10)

$$\theta = kP/(1+kP) \quad (2)$$

The intercept in this case suggests a second mode of SO_2 adsorption which may be determined by some surface

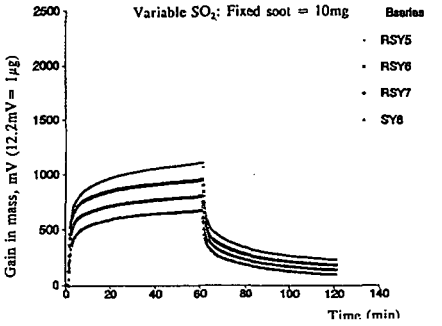

Figure 1. Adsorption of SO_2 on soot

characteristic. Independent evidence of another mode comes from Figure 1 in which the desorption of SO_2 by zero air asymptotically approaches a limiting mass reflecting retention of as much as 20% of the total adsorbed. A likely candidate for

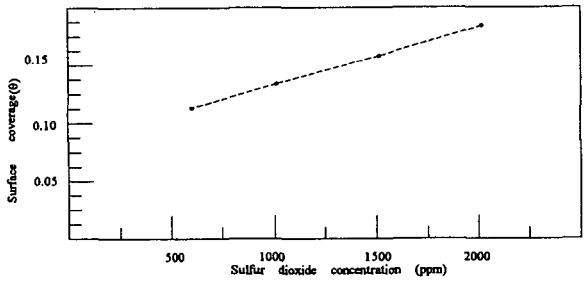

Figure 2. Plot of surface coverage (θ) as a function of P_{SO2}

this adsorption pathway is the surface hydrolysis of SO_2 to $SO_2.H_2O$ (H_2SO_3). The resulting reaction scheme

$$SO_2\ (g) + SS \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SS.\ SO_2\ (s) \quad (3)$$

$$SS.SO_2\ (s) + H_2O.ads \xrightarrow{k_2} SS.\ H_2SO_3\ (s) \quad (4)$$

where SS = surface site, could be followed by oxidation to sulfate

$$SS.H_2SO_3 + 1/2O_2 \xrightarrow{k_3} SS.\ H_2SO_4 \quad (5)$$

Small amounte of adsorbed water cannot be excluded from the soot surface under these conditions.

The effect of temperature on SO_2 adsorption was examined with a soot mass of 15 mg at 1010 ppm SO_2 by the same microgravimetric technique. Figure 3 shows a family of mass gain versus time curves over the temperature range 22°C to 66°C for the first 5

minutes of the adsorption experiment. These data represent surface coverages ranging from 8.6 to 2.2 percent, respectively, which exhibit a linear relationship to temperature. Utilizing microgravimetric data such as those of Figure 1, it is possible to estimate the fraction of adsorbed SO_2 which is irreversibly bound to the surface, as represented by equation 4,

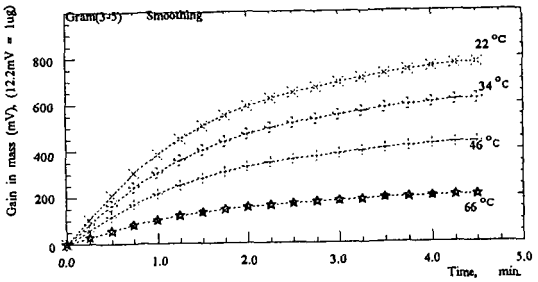

Figure 3. Mass gain versus time curves as a function of temperature.

at each temperature. From the total number of adsorbed molecules per gram, then, the reversibly adsorbed (physisorbed) SO_2 and a set of equilibrium constants for equation 3 have been calculated. These data are summarized in Table I.

Table I. Effect of Temperature on SO_2 Adsorption

Temperature, °C	SO_2 Surface Coverage, θ	Fraction of SO_2 physisorbed, f	$K_{eq} \times 10^{-16}$, molecules per g-ppm
22	0.0858	0.823	3.24
34	0.0684	0.810	2.54
46	0.0479	0.772	1.74
66	0.0225	0.763	0.79

Plots of $\log K_{eq}$ versus 1/T show some curvature reflecting the apparent fact that the enthalpy of physisorption for SO_2 on n-hexane soot is a function of surface coverage. Over the temperature range 22-66°C, this value averages 26.8 kJ/mol-K, a figure within the range of 20-27 kJ/mol found by Davini (11) for SO_2 adsorption on three oxidized carbons at 20°C and 1 atmosphere. By comparison, the molar heat of vaporization of SO_2 also is 26.8 kJ/mol at 22°C.

Coadsorption of SO_2 and NO_2

Spectroscopic and microgravimetric data from the NO_2/N_2O_4-soot system (1,2) over a wide concentration range conform to the Elovich equation, an isotherm for activated adsorption or chemisorption. The principal products at low concentration of NO_2 at laboratory temperatures are such functional groups as $-NO_2$, $-ONO$, $-NNO_2$. As noted above, on the other hand, SO_2 adsorption is primarily reversible, involves a low heat of adsorption and is more properly termed physisorption; however, up to 20% appears to be surface reactive or undergoes some type of chemisorption. Of interest in this work have been the molecular mechanisms of coadsorption of SO_2 and NO_2, given the different natures of their adsorption.

Figure 4 is a composite of microgravimetric curves of soot which summarizes its behavior during a series of SO_2 and NO_2 exposures.

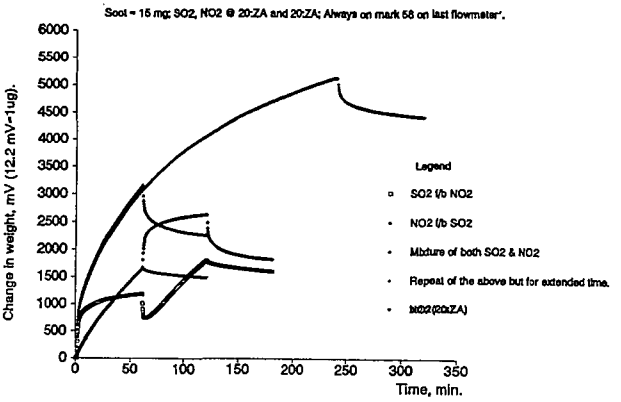

Figure 4. Adsorption of SO2 and NO2 on soot.

Each experiment was carried out with 15 mg soot and 1010 ppm of SO_2 and \ or NO_2 in zero air at 22°C. This sequence of curves reveals the following:

1. the typical SO_2 adsorption curve is interrupted by a flow of NO_2 at 60 min, the SO_2 desorption (as P_{SO2} --> 0) followed within 4 minutes by the increase in mass accompanying NO_2 chemisorption;
2. the inverse order of flow shows an adsorption of SO_2 following NO_2 of about 16% less than untreated soot; because NO_2 is mostly chemisorbed, the SO_2 flow does not result in visible mass loss.;
3. a flow of SO_2 and NO_2 together yields an increase in mass 11% higher than separately; this curve is reproduced over the longer term, with the loss of mass (mostly SO_2) about the same in each case when the same zero air purge is used;
4. small amounts of NO_2 are lost through zero air purge, indicating a small amount (9.7%) of NO_2 is loosely bound (physisorbed) under these conditions.

EPR measurements of spin density, the principles of which are discussed in our first symposium paper (8), have been carried out on this system as well, and the results are summarized in Figure 5. The decrease in corrected normalized integral (CNI) of soot's EPR signal with the pressure of paramagnetic NO_2 is evident as is the lack of effect of diamagnetic SO_2. When experiments in which SO_2 adsorption is followed by NO_2 adsorption and vice-versa are carried out, there clearly is no effect of the presence of SO_2 on the interaction of NO_2 with the unpaired electrons of soot. These data are consistent with the displacement of some adsorbed SO_2 by NO_2, however, as indicated by the microgravimetric data of Figure 4. This does not account for any presence of O_2 in zero air and its occupation of free radical sites, which would be reflected microgravimetrically in changes in capacity for SO_2 under some conditions.

Separate experiments have ehown that soot treated with 140 torr NO_2, resulting in a reduction of CNI from 1.62×10^7 to 0.61×10^7, undergoes an increase of 10% in unpaired spins upon exposure to air. Evacuation at 10^{-4} torr further increases the CNI to 1.05×10^7 while the addition of air returns it to 0.67×10^7, the cycle continuing to change the spin density of carbon in this manner. It appears that O_2 does compete effectively with the small physisorbed fraction (~10%) of adsorbed NO_2 for

unpaired electron sites.

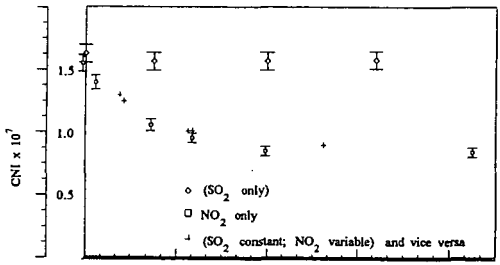

Figure 5. CNI against gas pressure

NO Adsorption

The FT-IR evidence presented for the lack of NO reactivity with soot at ambient temperatures (3) is supported by EPR studies of NO and NO + O_2 adsorption. Figure 6 shows the effects of O_2 and

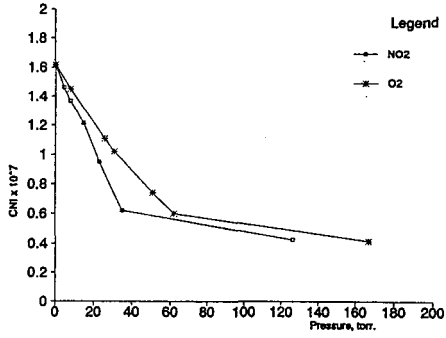

Figure 6. Effects of oxidants on the normalized integral of soot.

NO adsorption on the CNI of soot beyond a linear range below 50 torr to pressures of nearly 170 torr. The similar but slightly lesser effect of NO on spin density, as compared with that of O_2, forms the basis for the experiments summarized in Figure 7. Exposure of the soot to air following adsorption of NO at 8 and 62 torr shows the effect on CNI expected below and at / or above surface saturation by NO, respectively. The surprising effect is the more complete removal of paramagnetic species NO + O_2 to yield a higher CNI than the initial. This consistent result shows NO-assisted removal of that O_2 still remaining on the soot surface following the initial evacuation and mild thermal treatment. It is to be contrasted with the similar experiment with NO_2 described above. NO apparently is reversibly adsorbed and, probably through formation of a complex (or reaction) with pore O_2, even raises the spin density of the soot though its evacuation.

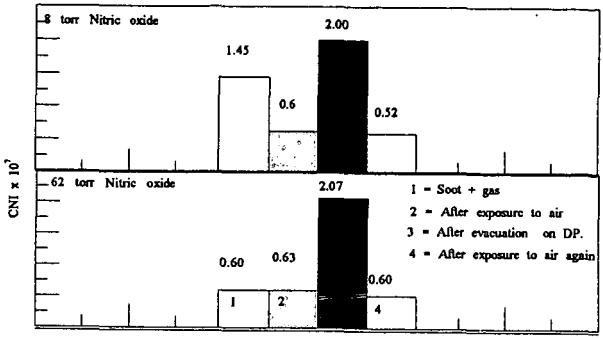

Figure 7 . Plot of CNI for Soot/gas-Air exposure-Evacuation-Exposure to air sequence .

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